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Assigning Reactive Excited States in Inorganic Photochemistry.

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Assigning Reactive Excited States in Inorganic Photochemistry

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The matter of assigning reactive excited states in inorganic photochemistry turns out to have complexities as more detailed and more varied information is obtained. Three cases are considered. For Cr(III) ammines there is still much controversy in the assignment of chemical reactivity to doublet and quartet states. In the case of $Rh(NH_3)_5X^{2+}$ complexes, it may be necessary to invoke three different reactive or emitting ligand field excited states, and in that of $W(CO)_5L$ species, at least two, including a charge transfer state, are needed.

Assigning Reactive Excited States in Inorganic Photochemistry

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Introduction

We are seeing currently the development of an extended research field for that special breed of physical inorganic chemist, the excited state kineticist. Studies of excited state rate processes are an increasingly important adjunct to conventional quantum yield and product characterizations. Increasingly complex and intimate excited state reaction schemes are being constructed. The identification of the reactant species, ordinarily obvious in thermal reactions, turns out not to be so obvious in excited state chemistry. We limit ourselves here to three examples, involving transition metal complexes in solution.

The general picture, and some vocabulary should be presented first. In the case of mononuclear complexes having monodentate or simple bidentate ligands, to which this discussion will be confined, the visible-uv absorption spectra show two principal types of transitions, ligand field, LF, and charge transfer, CT. They may be several LF absorptions, and we designate these as L_1^n, L_2^n, etc., with a left superscript to indicate the spin multiplicity of the terminal state. Thus the $^4A_{2g} \longrightarrow {}^4T_{2g}$ transition for a d^3 O_h complex is labelled $^4L_1$. Already there is a difficulty; spin and orbital angular moment increasingly mix on going to the heavier transition metals, and the use of spin-only designations, while convenient, is suspect.

LF bands are usually broad, and it is now generally accepted that the optical transitions are Franck-Condon in type, so that absorption of light gives a distribution of vibrationally excited molecules, which rapidly relax or thermally equilibrate to the temperature of the medium. The broad absorption band is essentially the Franck-Condon envelope for the transition. The _thexi_ state, as we will call the thermally equilibrated excited state, may have not only different metal-ligand bond lengths, but also different bond _angles_ (see Ref. 1). The classic indication of such distortion is the presence of a very large Stokes' shift in those Cr(III) complexes that show fluorescence.[2,3] Similar broad emission bands and large Stokes' shifts are observed for spin forbidden transitions as well, although the d^3 case is an exception. In the $^2L_1$ transition, there has merely been rearrangement of electrons in the t_{2g} set of orbitals; these are non-bonding, and little excited state distortion occurs so that the phosphorescence spectrum is narrow and vibronically structured, and not much displaced from the $^2L_1$ band.

Because of the distortion problem, we will avoid the use of orbital symmetry symbols in labelling LF thexi states. Rather, we designate them by their nominal spin multiplicity: S (singlet), D (doublet), T (triplet), and Q (quartet or quintet), with a right subscript to give the energy ordering, and a right superscript zero to denote thermal equilibration. The $^4T_{2g}$ ligand field state is labelled Q_{FC} (as a Franck-Condon state), and becomes Q_1° after thermal equilibration. States related by descent of symmetry from O_h may be designated by primes.

Again as noted earlier,[1] thexi states are good _thermodynamic_ species. An ensemble of such a species has entropy, free energy and a

standard redox potential, as well as energy. It is a topological isomer of the ground state just as square planar and tetrahedral ML_4 complexes are isomers. The thexi state is a good _kinetic_ species. Its reactions can be activated, stereospecific, subject to ionic strength effects, etc. Its intimate reaction mechanism should be treatable by conventional theories for rate processes. The identification of the reactive thexi state in inorganic photochemistry is thus a matter of serious chemistry.

The typical excited state processes with which we deal are illustrated in Figure 1, for the d^3 system. Q_{FC} may thermally equilibrate to $Q_1°$, or may undergo prompt intersystem crossing, _pisc_, to $D_1°$. The thexi states may exit by emission, of rate constant k_r, by non-radiative return to the ground state, k_{nr} and k'_{nr}, or by chemical reaction, k_{cr} and k'_{cr}. They may interconvert by intersystem crossing, _isc_, and back intersystem crossing, _bisc_. A non-classical chemical reaction is that which occurs during non-radiative relaxation--the so-called _hot ground state reaction_. These have been very difficult to establish, and will not be considered here.

We turn now to specific systems, to examine what progress has been made in identifying reactive states, and in obtaining actual rate constant values.

Cr(III) Ammines. - The photochemistry, essentially substitutional, has been studied extensively (see Refs. 4-6). The interesting situation is that after some twenty years of activity in the field, there are still questions as to the roles of $D_1°$, $Q_1°$, and, in the case of non O_h complexes, any $Q_1°'$. An early supposition was that _all_ reaction was from $D_1°$;[7,8] it was known as relatively long-lived state, typically with msec phosphorescence lifetimes at 77 K, and the spin pairing could free an orbital to facilitate a concerted substitution process. In seeking

to test the doublet hypothesis, we came to the conclusion that the $Q_1{}^\circ$ state could not be ignored, and produced the photolysis rules:[9]

Rule 1: Consider the six ligands to lie in pairs at the ends of three mutually perpendicular axes. That axis having the weakest average crystal field will be the one labilized, and the total quantum yield will be about that for an O_h complex of the same average field.

Rule 2: If the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates.

The rules are approximately obeyed, although there are exceptions (see Refs. 4, 5, 10), and made theoretical sense if $Q_1{}^\circ$ were the reactive state. From the ligand field point of view, an electron has been promoted to an e_g antibonding orbital and, in a non-O_h complex, the antibonding axis could be expected to be the one for which the average ligand strength was the weaker. In figure 1, provided that distortion has not significantly disturbed the octahedral framework, $Q_1{}^\circ$ would usually be the axially labilized thexi state in a C_{4v} complex, and $Q_1{}^{\circ\prime}$, the equatorially labilized one. More quantitative and more elaborate ligand field explanations have been made, which adequately predict both the rules and the exceptions to them.[10-12] At one point, it became widely thought that all reaction occurred from $Q_1{}^\circ$, but now the pendulum is swinging back a little.

Complexes of the type $Cr(NH_3)_5X^{2+}$ show two photoreaction modes, ammonia aquation and aquation of the X^- group. The absorption spectrum for $X^- = NCS^-$ is shown in Figure 2; this case provided an early indication that both $D_1{}^\circ$ and $Q_1{}^\circ$ are reactive,[13,14] both in that the ratio of

reaction modes changed with wavelength, and from sensitization results. A point of relevence later is that the ammonia photoquation, the rules-predicted mode, is <u>antithermal</u>, that is, the labilized ligand is not the thermally reactive one. In the case of <u>trans</u>-$Cr(en)_2(NH_3)(NCS)^{2+}$, <u>three</u> reaction modes have been reported,[15] aquation of one end of an ethylenediamine ligand, ammonia aquation, and (presumably) thiocyanate aquation. Are the excited states just being sloppy or are three different ones now involved?

A new leverage became available when it was found that D_1° emission could be observed in <u>room temperature</u> solution, with lifetimes now in the μsec or nsec region (indicating that k_r was no longer important).[16-19] The emission could be quenched (see Ref. 6), and an important observation was that on quenching the emission, much of the photochemistry is also quenched in the cases of <u>trans</u>-$Cr(NH_3)_2(NCS)_4^-$ [20] and $Cr(en)_3^{3+}$ [17,21,22] (but not for $Cr(CN)_6^{3-}$ [23]). D_1° is clearly implicated in the first two cases, and the simplest explanation of D_1° involvement is that it is chemically reactive and furnishes part of the overall quantum yield. Alternatively, however, promptly formed D_1° could be returning to Q_1° by <u>bisc</u>, so that all reaction is still from Q_1°.

In an effort to probe these alternatives, we monitored the rate of appearance of primary photoproduct, in the case of $Cr(en)_3^{3+}$, and found that indeed 30% of photoproduct, $Cr(en)_2(enH)(H_2O)^{4+}$, appeared in less than a few nsec, with the remainder growing in with the D_1° emission lifetime.[24] Because of ground state bleaching, it was also possible to determine the efficiency of D_1° formation and thence ϕ_D', the efficiency of the "slow" product formation. This was significantly

greater than the overall quantum yield, indicating that chemical reaction was indeed occuring from $D_1°$ as well as from $Q_1°$, see further below.

Further support for $D_1°$ as a reactive state has come from emission rules for room temperature solutions,[19] of which the second is:

Rule 2: If two different kinds of ligands are coordinated, the emission lifetime will be relatively long if that ligand which is preferentially substituted in the thermal reaction lies on the weak field axis of the complex.

Implied in the rule is that the emission lifetime, τ, is determined mainly by k_{cr}, rather than by k_{nr} or k_{bisc}. A rationale for the rule is that the reactivity of $D_1°$ tends to parallel that of the ground state; that the paralleling is in reaction rate as well as in reaction mode is indicated by some more recent observations.[25]
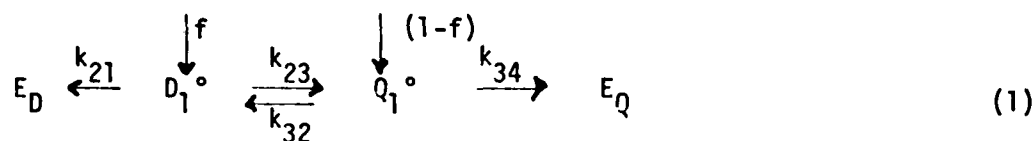
Our hypothesis at this point is that where the photolysis rules predict the thermal reaction mode (as for any O_h complex and for trans-$Cr(NH_3)_2(NCS)_4^-$), the photoreaction may partly be from $Q_1°$ and partly from $D_1°$, the latter being the quenchable portion. Where the photolysis rules predict an antithermal reaction, this is from $Q_1°$, while any thermal reaction mode present is from $D_1°$.

At present there is no consensus, and some specific contentions on the matter of $D_1°$ reactivity (note Refs. 17, 21, 22, 26-30). In addition, an alternative attempt to account for two reaction modes has been to invoke a $Q_1°'$, with ligand field analyses as to how axial and equatorial labilization should behave.[31]

The case of $Cr(en)_3^{3+}$. - We turn now to the specific case of aqueous $Cr(en)_3^{3+}$ to see how emission lifetime measurements can be helpful in assessing $D_1°$ reactivity (see also Ref. 32 for the case of trans-$Cr(NH_3)_2(NCS)_4^-$). If our interpretation is correct, $1/\tau$ gives k_{cr};

on the alternative hypothesis, $1/\tau$ is related to k_{bisc}.

We are dealing with a coupled reaction scheme, equation (1):

$$E_D \xleftarrow{k_{21}} \quad D_1^{\circ} \downarrow^f \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} \quad Q_1^{\circ} \downarrow^{(1-f)} \xrightarrow{k_{34}} \quad E_Q \tag{1}$$

Following an excitation pulse producing unit concentration of Q_{FC}, pisc occurs with efficiency $\underline{f}$, so that at small times (on the nanosecond time scale), we have $(D_1^{\circ})^{\circ} = f$ and $(Q_1^{\circ})^{\circ} = (1-f)$. The exiting rate constants are $k_{21} = k_r + k_{nr} = k_{cr} \simeq k_{nr} + k_{cr}$, and $k_{34} = k'_r + k'_{nr} + k'_{cr} \simeq k'_{nr} + k'_{cr}$, and the efficiency of chemical reaction from D_1° is $\phi'_D = k_{cr}/k_{21}$, while that from Q_1° is $\phi'_Q = k'_{cr}/k_{34}$. The intersystem crossing rate constants are denoted by k_{23} (bisc) and k_{32} (isc). In the case of quenching of D_1° emission, the exiting rate constant k_{21} is augmented by the term $k_q(A)$, where A is the acceptor or quenching species.

The solution to Equation (1) has been published,[33,34] and we proceed to the aspect of interest here. The rate at which exiting occurs from D_1° is $k_{21}(D_1^{\circ})$, and the total exiting up to time t is $E_D = k_{21} \int_0^t (D_1^{\circ})dt$. Analysis gives

$$E_D = \frac{k_{21}}{\lambda_2 - \lambda_1} \left\{ \frac{f(\lambda_2 - \alpha) + (1-f)k_{32}}{\lambda_1} (1-e^{-\lambda_1 t}) \right.$$
$$\left. - \frac{f(\lambda_1 - \alpha) + (1-f)k_{32}}{\lambda_2} (1-e^{-\lambda_2 t}) \right\} \tag{2}$$

where $\alpha = k_{21} + k_{23}$ and

$$2\lambda_{1,2} = (\alpha + \beta) \pm [(\alpha - \beta)^2 + 4k_{23}k_{32}]^{1/2} \tag{3}$$

where $\beta = k_{32} + k_{34}$, and λ_1 and λ_2 are the two observable decay constants

for the system (see Ref. 34 for an example of their measurement).
Similarly, the total exiting from $Q_1{}°$ is given by

$$E_Q = \frac{k_{34}}{\lambda_2 - \lambda_1} \left\{ \frac{f\, k_{23} + (1-f)(\lambda_2 - \beta)}{\lambda_1} \ (1 - e^{-\lambda_1 t}) \right.$$
$$\left. - \ \frac{f\, k_{23} + (1-f)(\lambda_1 - \beta)}{\lambda_2} \ (1 - e^{-\lambda_2 t}) \right\} \tag{4}$$

Equations (2) and (3) may be abbreviated

$$E_D = A(1 - e^{-\lambda_1 t}) + B(1 - e^{-\lambda_2 t}) \tag{5}$$
$$E_Q = C(1 - e^{-\lambda_1 t}) + D(1 - e^{-\lambda_2 t}) \tag{6}$$

and the total yield of photoproduct, ϕ, is just $E_D + E_Q$.

In the present case, λ_1 is a large number and λ_2 is unity, if time is measured in units of 1.8 microseconds (since the experimental emission lifetime, given by $1/\lambda_2$, is 1.8 μsec). At time small compared to $1/\lambda_2$, but large compared to $1/\lambda_1$, we have

$$\phi_{fast} = \phi_D' A + \phi_Q' C \tag{7}$$

Further product formation then grows in, the eventual additional yield being

$$\phi_{slow} = \phi_D' B + \phi_Q' D \tag{8}$$

The quenchable fraction of the total yield is ϕ_{slow}/ϕ.
Experimentally, $\phi = 0.37$,[5] $\phi_{fast} = 0.11$, and $\phi_{slow} = 0.26$. In addition, our monitoring results gave f = 0.30 (assuming that $(D_1°)°$ is formed by _pisc_).[24]

Suppose, as Regime IA, that $k_{bisc} = 0$. A possible set of _k_ values is given in case 1, Table I. Case 2 is for the maximum possible _f_ value, if ϕ_{fast} is not to drop below 0.11, and ϕ_D' is at its minimum allowable value of 0.29, which means that $k_{cr}/(k_{cr} + k_{nr}) = 0.29$ or

$k_{nr} \simeq 2.4\ k_{cr}$. The emission lifetime is given essentially by $1/k_{21} =$ $1/(k_{nr} + k_{cr})$, and we note that, experimentally, τ showed linear Arrhenius plots with an apparent activation energy of 10 kcal mole^{-1}.[19] Good Arrhenius behavior seems unlikely if two quite different kinds of rate constants are making comparable contributions. Case 1, with $\phi_D' =$ 0.87, or, were $\underline{f}$ slightly smaller, with $\phi_D' = 1$, is more acceptable in this respect. Analysis of this regime thus suggests that τ is indeed controlled mainly by k_{cr}.

Regime IB is one in which $(D_1°)°$ appears via $\underline{isc}$, $\underline{f}$ being zero. Case 3 in Table I gives an acceptable calculation in terms of the observables, but a numerical difficulty arises. If $D_1°$ is to appear within a few picoseconds, as it apparently does,[35,36] k_{32} must be about 10^{11} sec^{-1}, and k_{34} must also be of this magnitude if ϕ_{fast} is to be as large as 0.11. The energy difference between $Q_1°$ and $D_1°$ has been estimated to be about 13 kcal mole^{-1}.[37] *Neglecting entropy contributions*, $k_{23}/k_{32} = 3\times10^{-10}$ so that $k_{23} \dot= 30$ sec^{-1}, an uncomfortably small value. Regime IA is to be preferred over IB, but the latter cannot be ruled out.

In Regime IIA, we suppose that $k_{cr} = 0$ ($k_{21} = k_{nr}$), so that all chemical reaction is via $\underline{bisc}$ and $Q_1°$; this is the alternative hypothesis. The emission lifetime is now related to k_{23}, which is therfore taken to be about unity in Table I, case 4. This case is acceptable as to ϕ_{fast} and ϕ_{slow}, but requires the yield of $(D_1°)°$ to be 0.7, contrary to our observation of 0.3; no lower value for this yield can be found in this regime. There are again numerical difficulties. The regime requires that k_{nr} not be much greater than k_{23} since k_{nr} is a wasting process. *This is unlikely since both reactions are non-radiative transitions, but with less geometry change, and* $\underline{no}$ *spin change for* k_{nr}. In addition, little activation energy is expected for k_{nr}, while k_{23} must now be

assigned the 10 kcal mole^{-1} barrier obtained from the temperature dependence of τ. Also, since $k_{23} \approx 1/\tau \approx 0.5 \times 10^6$ sec^{-1}, we find $k_{32} \approx$ $0.5 \times 10^6 / 3 \times 10^{-10} \approx 2 \times 10^{15}$ sec^{-1}. This is much too fast. Even if the energy gap between $Q_1{}^\circ$ and $D_1{}^\circ$ is reduced to the minimum value of 10 kcal mole^{-1} (set by the temperature dependence of τ), k_{32} is still about 1×10^{13} sec^{-1}, which in turn implies an equally uncomfortably large value of k_{34}. Regime IIB, in which $(D_1{}^\circ)^\circ$ is produced by isc rather than by pisc, runs into similar difficulties.

Although the above presentation has been sketchy, it illustrates the point that quantitative considerations can limit the type of kinetic scheme that is acceptable. In the case of Cr(en)$_3{}^{3+}$, the result is a distinct favoring of Regime IA, namely chemical reaction from $D_1{}^\circ$ formed by pisc.

Rh(NH$_3$)$_5$X^{2+} complexes. - We take up briefly two more types of complexes. The photochemistry aqueous of Rh(III) ammines is mostly substitutional (see Refs. 38-41). Rh(NH$_3$)$_5$Cl^{2+} photoaquates Cl$^-$ with $\phi = 0.16$ at 350 nm, while Rh(NH$_3$)$_5$Br^{2+} shows both ammonia photoaquation, $\phi_{NH_3} = 0.18$ and bromide aquation, $\phi_{Br} = 0.019$.[42] Emission from aqueous solutions has recently been observed,[43,44] and may be quenched by OH$^-$ ion.[45,46] On quenching the emission, we found that ϕ_{Cl} was 85% quenched, in the case of Rh(NH$_3$)$_5$Cl^{2+},[45] and that ϕ_{NH_3} was fully quenched, but ϕ_{Br}, not at all, in the case of Rh(NH$_3$)$_5$Br^{2+}.[46]

An interesting and important problem is now posed. Conventional wisdom assigns the emitting state as a triplet and since the emission spectra and lifetimes are very similar for the two complexes, it would seem that it is the same triplet state in both cases, which we call $T_1{}^\circ$. A simple explanation of the quenching results is that $T_1{}^\circ$ is chemically reactive, but if this is so, then Rh-Cl bond breaking occurs in the one case, and

$Rh-NH_3$ bond breaking in the other. The bromide mode of reaction can then be assigned to some other state, say $T_1^{\circ\prime}$, as illustrated in Figure 3a. Although ligand field rationalizations can be made, it seems awkward to ask that the chemical reaction mode make so complete a change between $X = Cl^-$ and $X = Br^-$.

An alternative scheme, shown in Figure 3b, invokes three excited states. The bromide yield is assigned to a quinted state, Q_1°, and the quenchable photochemistry to T_1° or to $T_1^{\circ\prime}$, whichever is the lower lying, but with the emission from T_1° in both cases. [The quinted state is not necessarily high in energy in C_{4v} ligand field theory (see Ref. 47).] Q_1° is placed with less distortion than T_1° because of its more symmetric arrangement of anti-bonding electrons, and might be similar to D_1° in d^3 systems in having ground state-like reactivity.

At present, no decision seems possible between the two and the three reactive state schemes. The former has been suggested,[48] but from data that do not rule out the alternative:

$\underline{W(CO)_5L \text{ complexes}}$. - Another d^6 situation is that of group VI carbonyl compounds. $W(CO)_5L$ complexes, where L is a n-electron donor undergo photodissociation of the L ligand, and in the presence of a second ligand, L', the intermediate $W(CO)_5$ is scavenged to yield $W(CO)_5L'$.[49,50] The quantum yield for such reactions is ordinarily several tenths, but as L becomes more electron withdrawing, a CT band moves to the long wavelength side of the first LF band, and the yield drops to around 0.02.

For the case of L = 4-cyanopyridine, we observed emission in room temperature methylcyclohexane solution with 0.1 M ethanol present as L' (as well as without the ethanol).[51] The emission was quenchable by

anthracene, for example, and on quenching the emission, the photoproduction of $W(CO)_5$ (ethanol) was also quenched. Clearly the emitting state, possibly a triplet charge transfer, ^3CT, state, is implicated in the photochemistry. We can write $\phi = k_{cr}/(k_r + k_{nr} + k_{cr})$ for this state and, since ϕ is small, $\phi \simeq k_{cr}/k_{nr}$; k_r is taken to be negligible. The temperature dependence of ϕ gives an apparent activation energy of 7.6 kcal mole^{-1}, so if ^3CT is both the reactive and the emitting state, $7.6 = E_{cr}^* - E_{nr}^*$. In the one-reactive state scheme, Figure 4a, $1/\tau = (k_r + k_{nr} + k_{cr}) \simeq k_{nr}$, and from the temperature dependence of τ, $E_{nr}^* \simeq 1.5$ kcal mole^{-1}, whence $E_{cr}^* = 9.1$ kcal mole^{-1}. This may be high for what is thought to be a simple bond dissociation reaction.

An attractive alternative is a two-state scheme in which chemical reaction occurs from a LF state lying above the emitting CT one, and in steady state equilibrium with it, as shown in Fig. 4b. The observed E_ϕ^* is now attributed primarily to the energy difference, ΔE, between the two states. In this scheme, excitation leads, through intersystem crossings to ^3CT. This state is emitting, but not highly chemically reactive. The higher LF state, presumably $T_1°$, does react efficiently, but the overall quantum yield is low because of the competition with non-radiative relaxation of ^3CT. If L is such that $T_1°$ is the lower lying state, then the quantum yield should be large, as observed.

The two-state scheme has been favored,[49,52,53] also a similar one has been proposed for $Ru(NH_3)_5L^{2+}$ complexes.[54] Quantitative considerations indicate at least some caution, however. In the two-state scheme, k_{bisc} must compete with k_{nr}, and the emission lifetime of 360 nsec at 25 °C gives $k_{nr} \simeq 2.8 \times 10^{+6}$ sec. We have $\Delta E = E_\phi^* + E_{nr}^* - E_{cr'}^* = 9.1 - E_{cr'}^*$, where $E_{cr'}^*$ is the activation energy for reaction from $T_1°$, which is probably small. If we take ΔE to be the full 9 kcal mole^{-1}, and suppose that $k_{bisc} \simeq 0.1 \, k_{nr}$, then

$2.8 \times 10^{+6} \times 0.1 = A_{bisc} \exp(-9,000/RT)$, whence $A_{bisc} = 1 \times 10^{12}$ sec^{-1}. No allowance has been made for entropy change, and this A_{bisc} value, while marginally acceptable, is a bit large. Further study of the $W(CO)_5L$ complexes is needed.

Summary and conclusions. - The three cases described here illustrate one of the problems for the excited state kineticist. His colleague who deals with ground state reactions usually knows what the reactant species is. The photochemist spends much effort in trying to find out what his reactants actually are, and in few cases so far has this effort been unambiguously successful. That is, while reasonable guesses provide good working hypotheses, it has been a difficult matter to be sure whether one is dealing with a one-reactive state scheme, or a two- or three-reactive state one. Determining the thexi state spin multiplicity and its actual structure is yet more difficult. Fast magnetic susceptibility methods may help on the former question, and also photochemistry in high magnetic fields. The structure problem may yield to excited state resonance raman spectroscopy (note Ref. 55)

An important reason for establishing at least the number of reactive thexi states in a given system is that ligand field theoreticians have been interested in explaining thexi state reactivity in terms of specific metal-ligand bond labilization leading to dissociation and a five coordinate intermediate (see Refs. 10-12). In such analyses, it makes a difference in d^3 if the state is D_1° or Q_1°, and, in d^6, whether it is S_1°, T_1°, Q_1°, or ^3CT. It can be embarrassing to provide a theoretical explanation for the wrong scheme! The mechanism of thexi state reactions has not been a focus of this paper. My personal opinion, however, is that the solvation reactions are more likely to be concerted with solvent than limiting dissociative in type.

Acknowledgement

Table 1

Case	$\dfrac{k_{21}}{k_{23}}$	$\dfrac{k_{32}}{k_{34}}$	f	$\dfrac{\lambda_1}{\lambda_2}$	B^a	C	D	$\dfrac{\phi_D'}{\phi_Q'}$	$\dfrac{\phi_{slow}}{\phi_{fast}}$	$(D_1^\circ)^\circ$
1.	$\dfrac{1}{0.01}$	$\dfrac{0.01}{1000}$	0.3	$\dfrac{1000}{1.01}$	0.297	0.700	0.003	$\dfrac{0.87}{0.16}$	$\dfrac{0.26}{0.11}$	0.30
2.	$\dfrac{1}{0.01}$	$\dfrac{0.01}{1000}$	0.89	$\dfrac{1000}{1.01}$	0.881	0.110	0.009	$\dfrac{0.29}{1.00}$	$\dfrac{0.26}{0.11}$	0.88
3.	$\dfrac{1}{0.01}$	$\dfrac{429}{1000}$	0	$\dfrac{1429}{1.01}$	0.298	0.700	0.002	$\dfrac{0.87}{0.16}$	$\dfrac{0.26}{0.11}$	0.30
4.	$\dfrac{0.01}{1}$	$\dfrac{0.01}{1000}$	0.7	$\dfrac{1000}{1.01}$	0.007	0.300	0.694	$\dfrac{0}{0.37}$	$\dfrac{0.26}{0.11}$	0.70

(a) The quantity A, Equation (5), is always a small number in these regimes.

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Legends for the Figures

Figure 1.   Energy vs. distortion diagram for a d^3 system. Bars locate

thexi states, indicated in square frames. Vertical lines denote

radiative and wavey lines, non-radiative processes. The light

horizonal lines indicate successive vibrational wells as the

solvent cage adjust to geometry changes (for clarity, shown only for

the thermal equilibration of Q_{FC}). (See Ref. 1).

Figure 2.   Absorption spectrum for $Cr(NH_3)_5(NCS)^{2+}$. (From Ref. 5).

Figure 3.   Energy vs. distortion diagram for $Rh(NH_3)_5X^{2+}$. (a) Two reactive

or emitting states. (b) Three reactive or emitting states.

Figure 4.   Energy vs. distortion diagram for $W(CO)_5L$. (a) Reactive and

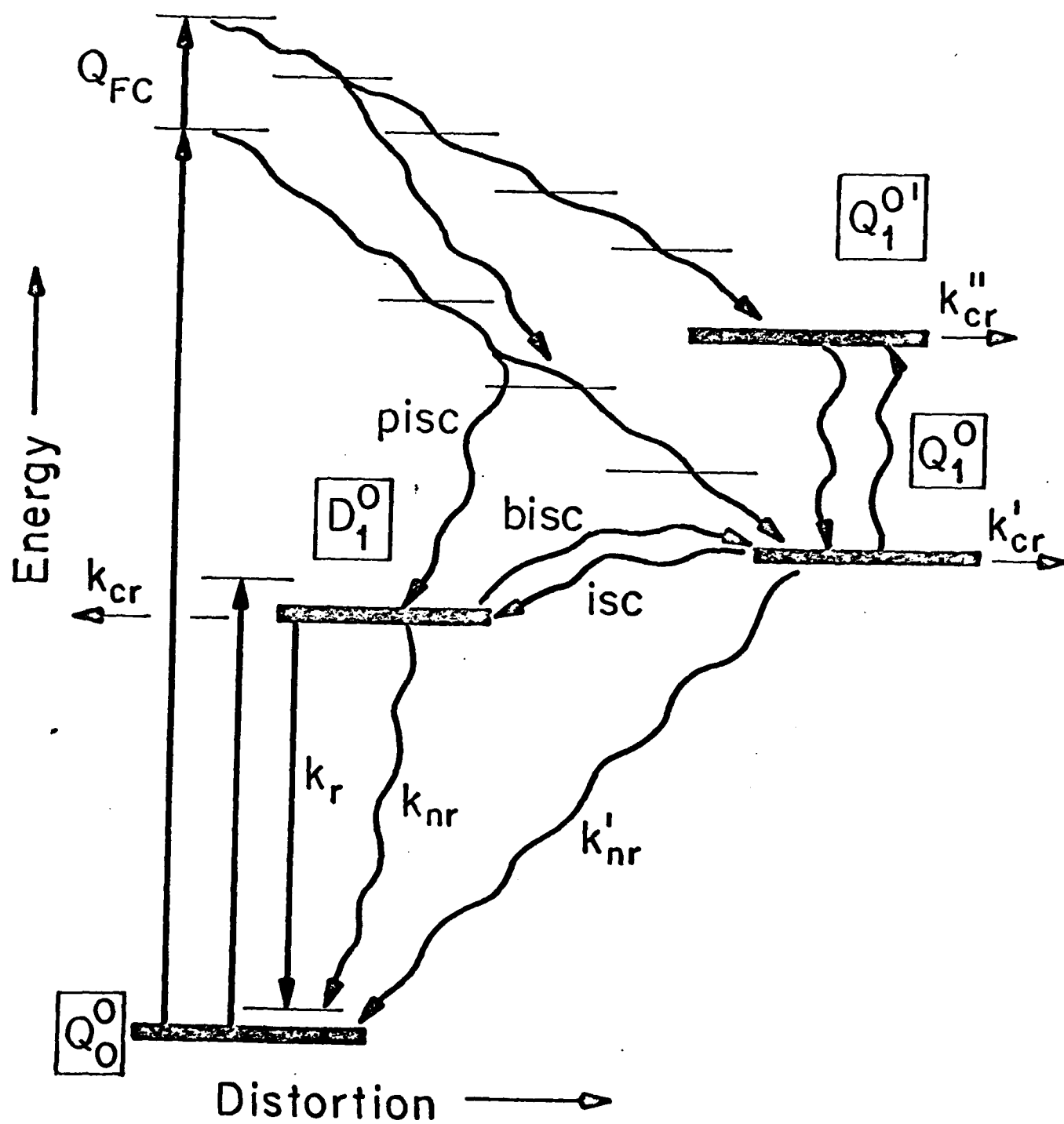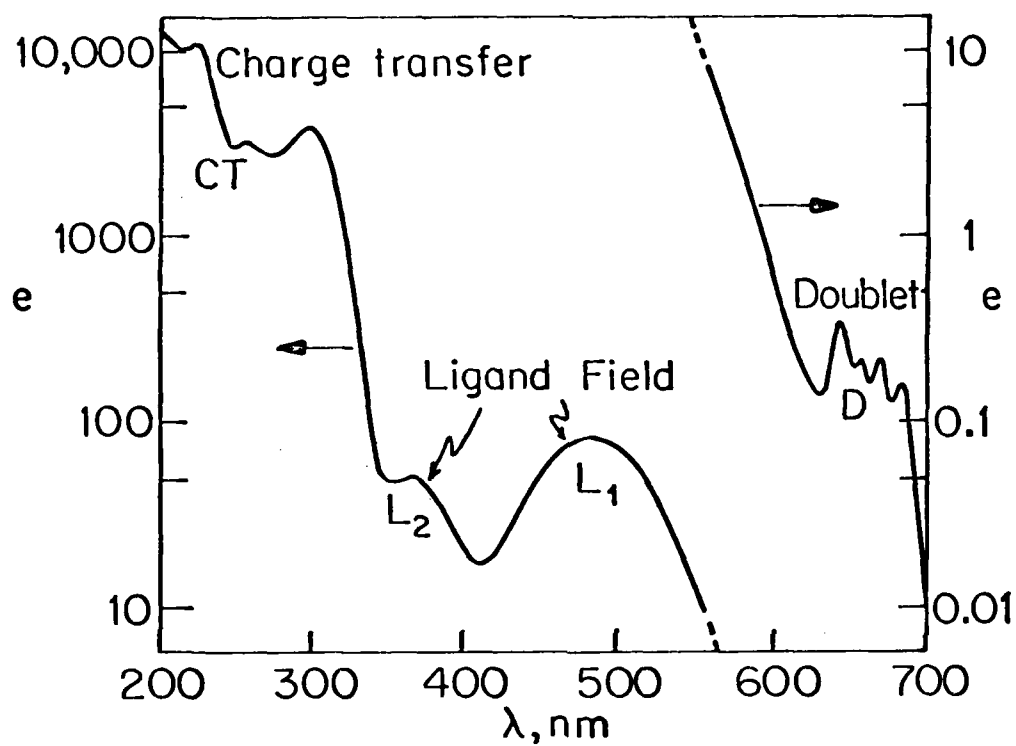emitting state the same. (b) Emission from ^3CT and reaction from

back-populated $T_1°$.

Figure 1

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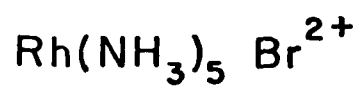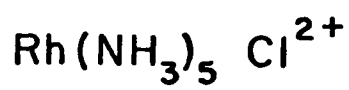
Figure 2

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(a)

S_1^0

T_1^0

$T_1^{0'}$

$Cl^- \leftarrow$

Cl^-

S_0^0

S_1^0

T_1^0

$T_1^{0'}$

$NH_3 \leftarrow$

Br^-

S_0^0

(b)

S_1^0

$T_1^{0'}$

Q_1^0

Cl^-

T_1^0

$\leftarrow$

Cl^-

S_0^0

S_1^0

Q_1^0

Br^-

T_1^0

$T_1^{0'}$

NH_3

S_0^0

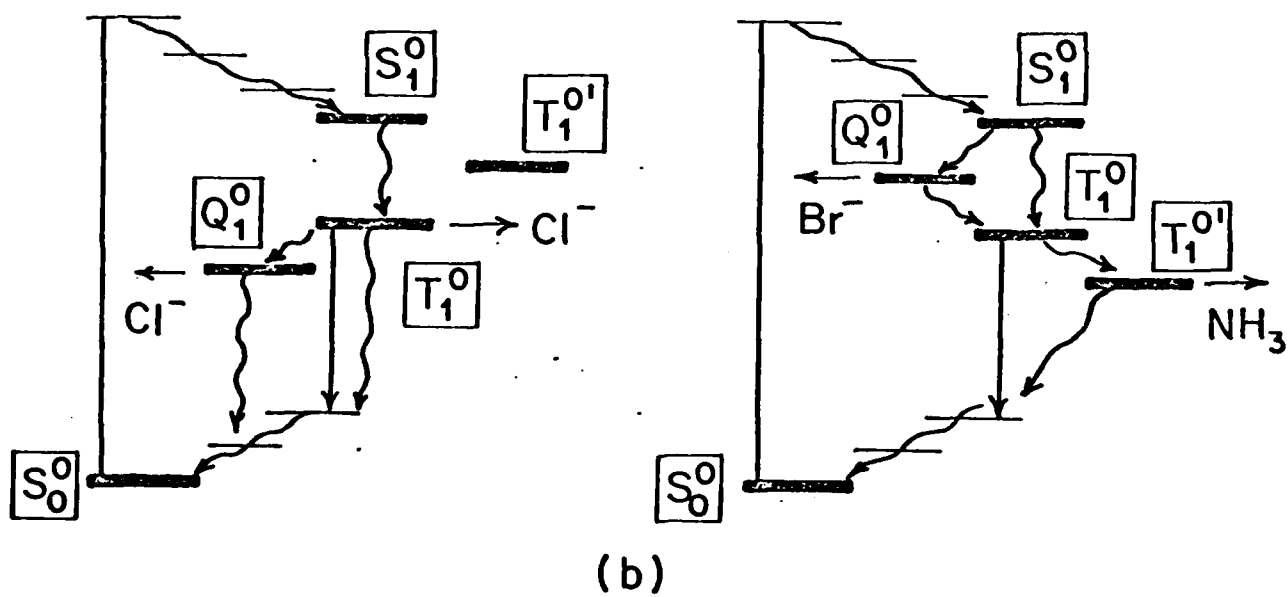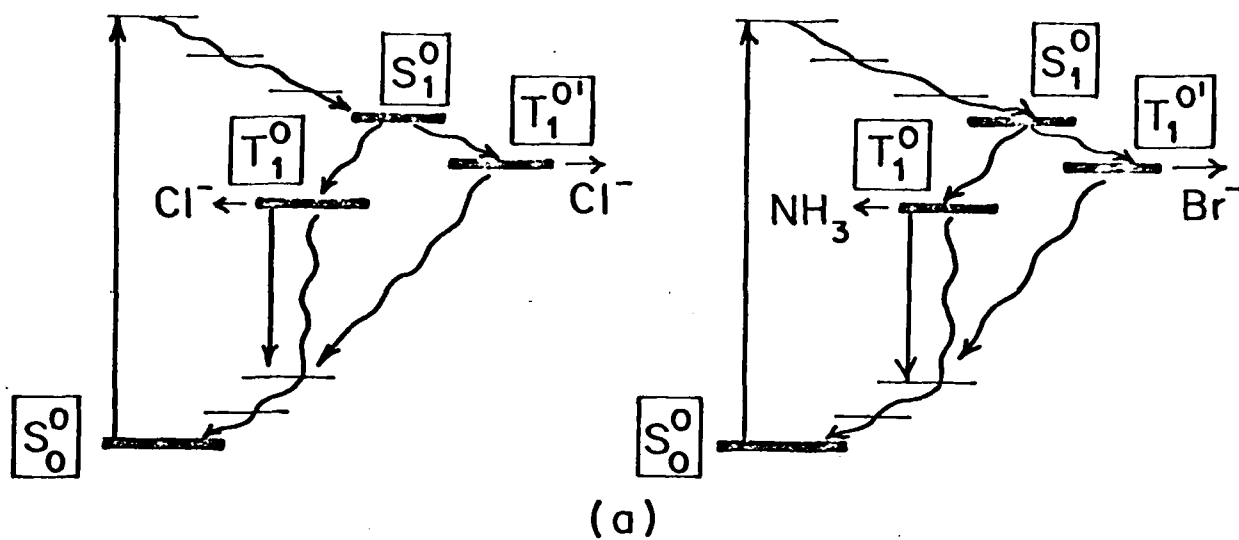$Rh(NH_3)_5 \, Cl^{2+}$

$Rh(NH_3)_5 \, Br^{2+}$
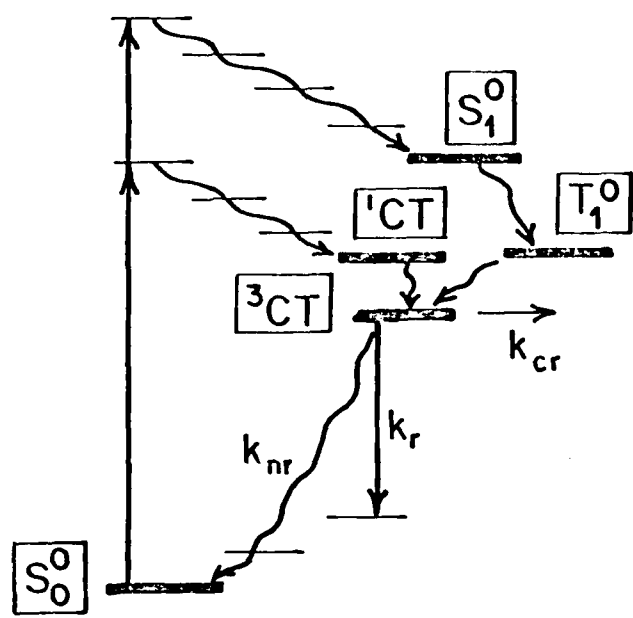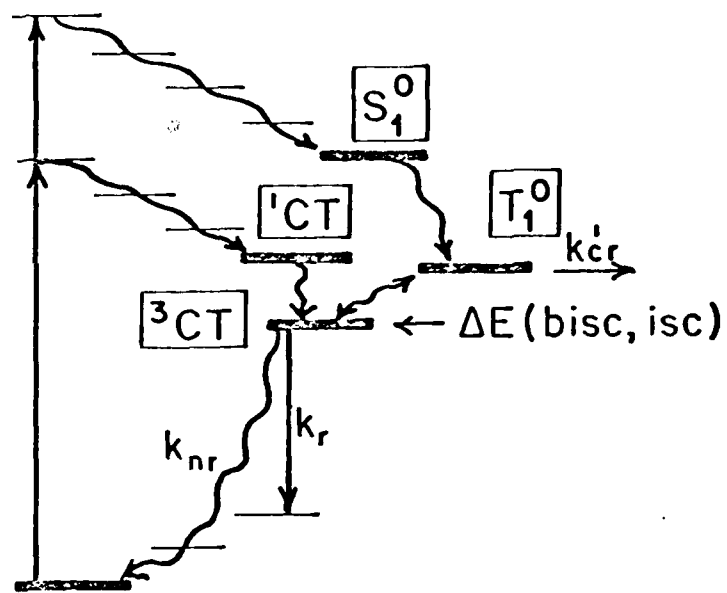
Figure 3

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(a)

(b)

Figure 4

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